

**VOLATILIZATION, OFF-SITE DEPOSITION,
DISSIPATION, AND LEACHING
OF DCPA IN THE FIELD**

January, 1989

**Environmental Hazards Assessment
Program**



**STATE OF CALIFORNIA
Department of Food and Agriculture
Division of Pest Management, Environmental Protection and Worker Safety
Environmental Monitoring and Pest Management Branch
1220 N Street, Sacramento, California 95814**

EH 89-2

**VOLATILIZATION, OFF-SITE DEPOSITION, DISSIPATION,
AND LEACHING OF DCPA IN THE FIELD**

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JANUARY 1989

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

ABSTRACT

Residues of dimethyl 2,3,5,6-tetrachloroterephthalate (DCPA) have been found repeatedly in recent years on a variety of produce grown in California to which this herbicide had not been applied. In response to this problem, drift, volatilization, dissipation, and leaching of DCPA were investigated in a circular plot seeded with onions, and off-site deposition was measured in a surrounding area seeded with parsley. Contamination by residual soil residues remaining on field after harvest was also examined by re-seeding the circular plot with parsley. Atmospheric residues detected downwind on resin and filters indicated DCPA moved off-target as a vapor as well as on particles both during and up to 21 d after application. Volatilization flux, measured using the aerodynamic method, reached a maximum rate of $5.6 \text{ g ha}^{-1} \text{ h}^{-1}$. An estimated 10% of the DCPA applied was lost to the atmosphere by volatilization within 21 d of application. Deposition of DCPA outside the circular plot was evidenced by residues found on potted parsley plants and soil set out up to 23 m from the treated plot. Parsley, seeded around the circular plot at the time of application and sampled 63 d later, contained residues ranging from 51 to 250 ug kg^{-1} indicating DCPA continued to move off-target in air up to two months after application. The mass of DCPA in soil exhibited a log-linear decline from which a 54 d half-life was calculated. Leaching of DCPA was minimal with residues found 122 cm deep, 21 d after application but was not found below the soil surface 168 and 336 d after application. Parsley planted in the circular plot after the onion harvest did not contain DCPA residues when sampled 217 and 336 d after the original application. Results indicated that drift during, and volatilization and subsequent atmospheric transport after application are potentially important sources of DCPA contamination occurring on non-target crops in California.

Acknowledgements

The authors would like to extend their appreciation to personnel from the California Department of Food and Agriculture for their tireless efforts in sample collection and chemical analysis. Air sampling, analysis, and flux calculations were done by personnel from the University of California at Davis under contract with CDFA. Special thanks to Mike Mata for field plot preparation and maintenance, without whose help, none of this would have been possible.

DISCLAIMER

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INTRODUCTION

The California Department of Food and Agriculture (CDFA) routinely analyzes produce samples to ensure that they do not contain pesticide residues exceeding established tolerance levels. For the past few years, residues of the herbicide dimethyl 2,3,5,6-tetrachloroterephthalate (DCPA) have been found repeatedly on a variety of produce samples to which it had not been applied. From 1984 through 1986 CDFA collected and analyzed 324 parsley samples, 16% of which contained residues of DCPA with concentrations ranging from 20 to 310 $\mu\text{g kg}^{-1}$ (CDFA, 1984-6). During the same period, 10, 37, and 11% of the daikon, dill, and kohlrabi samples were positive for DCPA, respectively. Since DCPA is not registered for use on these crops, tolerance levels have not been established (Code of Federal Regulations, 1987). When residues are found on crops which do not have an established tolerance, the crop is restricted from entering commerce (Gregory, 1987). Due to the occurrence of DCPA residues on parsley and other produce, and subsequent economic impact on growers, an investigation into the mechanism of off-target contamination was undertaken.

Pesticide drift during application and subsequent deposition on non-target crops has long been recognized as a mechanism of off-target movement (Akesson and Yates, 1964). Volatilization after application is also considered a major mechanism of pesticide movement from treated areas (Cliath et al., 1980; Seiber et al., 1986). It has been estimated that these two mechanisms account for 90% of the pesticide contamination occurring in air (Lewis and Lee, 1976). Therefore, local drift during, and volatilization after application were considered possible mechanisms of DCPA contamination occurring on produce grown in California.

The relatively long persistence of DCPA in soil might also be a contributing factor. The half-life of DCPA in soil was estimated to be between 40 and 100 days (Walker 1978; Hurto et al., 1979) with residues persisting up to 12 months after application (Miller et al., 1978). In certain areas of California with a long growing season, parsley and other crops can be rotated every few months. Consequently, DCPA found on such produce might also be from prior, legal applications causing contamination through transport to plant surfaces via raindrop splash and soil erosion (Pinder and McLeod, 1988) or through plant uptake of soil residuals. Therefore plant uptake and deposition on plant surfaces were also considered in this investigation.

This study was conducted to determine which of the above mechanisms: drift, volatilization and subsequent deposition downwind, windblown particles, and/or plant uptake, are responsible for DCPA contamination of nontarget crops. Drift, volatilization, dissipation, and leaching were examined in a circular plot planted with onions; surrounded by a crop of parsley. In addition, parsley was rotated into the circular plot about one month after the onion harvest to examine potential contamination by DCPA residues remaining in soil. Two DCPA metabolites, monomethyl 2,3,5,6-tetrachloroterephthalic acid (MTP) and 2,3,5,6-tetrachloroterephthalic acid (TPA) were included in the analysis to provide a mass balance accounting of the fate of DCPA in the field.

MATERIALS AND METHODS

Study Site

The study site was a 2.02 ha field located on land assigned to the Department of Land, Air and Water Resources at the University of California, Davis. Volatilization, soil dissipation and downward movement of DCPA was measured in a circular plot (100 m in diameter, Fig. 1). The circular design allowed for equidistant monitoring of the movement of DCPA off-site, regardless of wind direction. Soil type was characterized as a Yolo fine-silty, mixed, nonacid, thermic Typic Xerorthents with 1.2 to 1.4% organic matter and 29% sand, 46% silt, and 25% clay (Huntington et al., 1981). Portions of the field had been treated with DCPA in 1982 and 1984; DCPA was detected in background soil sampled prior to this study and ranged from none detected (detection limit 20 ug kg^{-1}) to 44 ug kg^{-1} .

On 7 and 8 April 1987 bunch onions (Allium cepa (L.) var. white lisbon), a crop with registered DCPA use, were planted ($13.5 \text{ kg of seed ha}^{-1}$) in the circular plot. At the same time, parsley (Petroselinum crispum (Mill.) Mansf. var. green modified curl leaf), a crop with no registered DCPA use, was planted ($5.6 \text{ kg of seed ha}^{-1}$) in the outer plot. Both crops were planted in raised beds 0.61 m apart. A 75% wettable powder formulation of DCPA was applied to bare soil of the circular plot on 9 April at a measured rate of 7.08 kg ha^{-1} using a tractor-mounted boom sprayer. Pertinent physical properties of DCPA are listed in Table 1. Crops were sprinkler-irrigated as needed, beginning one day after application. Onions were harvested on 7 July, 89 d after application. On 13 August (126 d after application) beds in the circular plot were reshaped, re-seeded with parsley and treated on 17 August with liquid prometryn (1.1 kg ha^{-1}) for weed control.

- Air Samplers
- x Soil Screens and Potted Parsley Plants
- Flux Sampling Mast

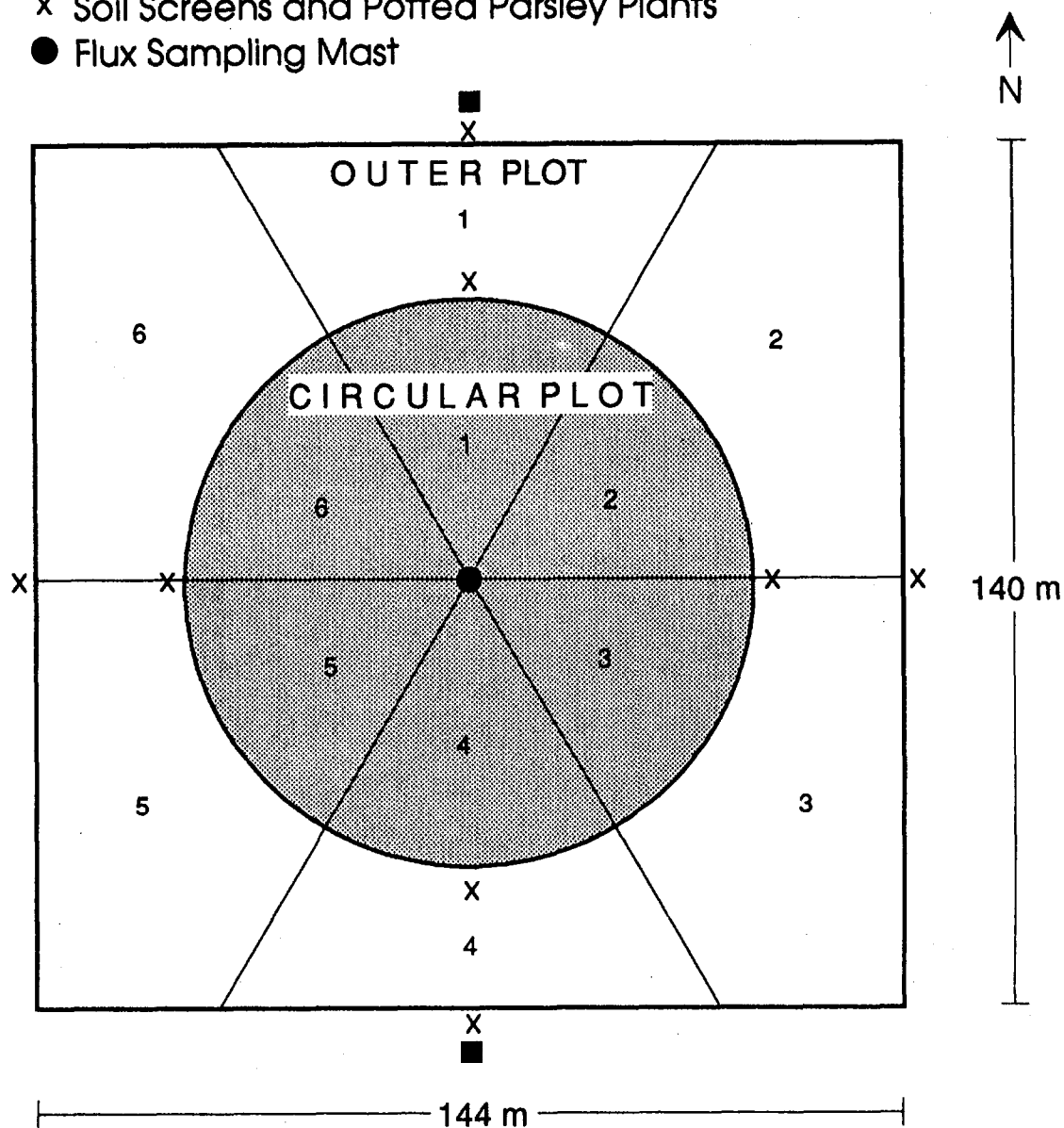


Figure 1. DCPA was applied to the circular plot (radius = 50 m) on 9 April 1987 at a measured rate of 7.08 kg ha^{-1} . Samples were collected from sections (numbered 1 - 6) in the circular and outer plots.

Table 1. Some physical properties of DCPA reported in the literature.

Molecular		Vapor	Henry's Law	K_{oc}
Weight	Solubility ^a	Pressure ^b	Constant ^c	(silty loam) ^d
332	0.5 mg L ⁻¹	3.3 x 10 ⁻⁴ Pa	2.2 x 10 ⁻⁶	3200

a. The Agrochemicals Handbook, Oct. 1983.

b. DePablo, R.S. 1981. J. Chem. Eng. Data 26:237

c. Calculated from solubility and vapor pressure.

d. Personal communication, Brian Korsch, Ricerca, Inc., Painesville, OH.

On the day of application, winds were out of the north with speeds between <1 and 6.4 m sec^{-1} , and temperatures ranged from the daytime high of 28°C (19% relative humidity (RH)) to a low of 4°C (91% RH). Between 10 April and 10 May 1987, winds were predominantly out of the north or south with speeds ranging from 1.0 to 6.9 m sec^{-1} . Daytime highs averaged 29°C and lows 9°C , with high average RH 85% and low 21%.

Measured Application Rate

Sheets of plastic-backed absorbent paper, 929 cm^2 , were used to measure DCPA deposition in the circular plot. Two sheets were placed at randomly selected locations in each section of the circular plot ($n=12$). The measured rate of application, 7.08 kg ha^{-1} , was close to the theoretical application rate of 6.71 kg ha^{-1} .

Air Sampling

Air samples were collected 30 m upwind and downwind of the circular plot (Fig. 1) on 0 through 4, 8, 11, 14, and 21 d after application, to coincide with flux sampling periods (see below). Air samples were collected using 100 mL of XAD-4 resin ($0.84 - 0.297 \text{ mm}$ [20 to 50 mesh], Rohm and Haas, Philadelphia, PA) preceded by a 20 by 25 cm glass fiber filter in high volume air samplers with flow rates of $1 \text{ m}^3 \text{ min}^{-1}$. Resin and filters were used to roughly distinguish between vapors and particles. Upwind concentrations were below the detection limit (0.5 ng m^{-3}), indicating that external sources of DCPA did not influence results.

Flux-air samples were drawn through 30 mL of XAD-4 resin in low volume samplers operating at 50 l min^{-1} . Flux sampling began 10 h after application and proceeded almost continuously through day 2, and also intermittently on 3, 5, 8, 11, 14, and 21 d after application (Appendix

1). The aerodynamic method (Taylor 1978) modified by Majewski et al. (1989) was used to calculate evaporative flux from air concentrations and wind speed data. Flux samples were collected using a 1.5 m mast located in the center of the circular plot (Fig. 1). Air samples and wind speed measurements were taken at 20, 35, 55, 90, and 150 cm above the soil surface. Flux was then calculated as the product of concentration and wind gradients divided by a meteorological stability factor (Appendix II).

Off-target Deposition

Soil screens (consisting of 4x10 cm wire mesh covered with a layer of soil) and potted parsley plants were placed in the outer plot at four compass points (N, E, S, and W) and two distances (3 and 23 m) from the edge of the circular plot to assess off-target deposition (Fig. 1). Samples were collected from each site -1, 0, 5, 10 and 91 d after application.

Soil and Vegetation Sampling

The circular and outer plots were each divided into six sections for soil and vegetation sampling (Fig. 1). Surface soil samples were collected -1, 0, 1, 7, 14, 21, 42, 63 and 84 d after application from each of the 12 sections. Additional soil samples were collected from the circular plot only on 168, 217 and 336 d after application. Each sample was a composite of four randomly collected soil plugs, 7.6 cm deep, collected with a stainless steel cylinder (4.13 cm, id).

Soil core samples were collected from three randomly selected sites in the circular plot -1, 1, 21, 84, 168 and 336 d after application using stainless steel bucket augers (6.83 or 7.9 cm id). Cores were collected

in successive 15.24 cm segments to a depth of: 305 cm before the study began (background), 30 cm one d after application and 152 cm during the remainder of the study. Bulk density determinations were made from a single 305 cm deep core collected in successive 15.24 cm segments using a stainless steel auger (3.49 cm id) specifically designed for bulk density sampling.

Vegetation samples consisted of 100 g of above-ground parts only. Each sample was a composite of four randomly collected sub-samples from each section. Onions were collected from the circular plot 42, 63, and 84 d after application. Parsley was collected from the outer plot 63 d after application and from the parsley crop, rotated onto the circular plot, 217 and 336 d after application (91 and 210 d after re-seeding).

Chemical Analysis

Air Samples

Resin from high volume samplers was extracted by shaking for 30 min with 150 mL of ethyl acetate. Ethyl acetate was decanted and filtered through Whatman paper no. 1 into a 500-mL round bottom flask. Ethyl acetate (100 mL) was added twice more and swirled for 15 and 10 min, followed by decanting and filtration. Combined extracts were rotoevaporated, transferred to a volumetric flask and analyzed for DCPA by gas chromatography (GC) using a Hewlett-Packard (HP) 5730A equipped with a ^{63}Ni electron-capture detector and a 30 m megabore column (J and W Scientific, DB-1). The carrier gas (argon/methane, 90:10 by volume) flow rate was 40 mL min^{-1} . Column, injector, and detector temperatures were 220, 250, and 300°C , respectively.

Resin from low volume samples was extracted as above with the exception that 50 mL of ethyl acetate was used for all three extractions. Analysis was performed by GC as for high volume samples. Mean recovery of DCPA from resin samples was $103 \pm 7\%$.

Glass fiber filters were cut into a 125-mL Erlenmeyer flask with 100 mL methanol plus one drop concentrated HCl. Samples were extracted by blending with a Tissuemizer for 1 min. Methanol was decanted and filtered through glass wool into a 250-mL round bottom flask. An additional 50 mL of methanol was added to the Erlenmeyer flask and the sample reblended for 1 min. The solvent was decanted, filtered, and combined, then evaporated to dryness. Samples were quantitatively transferred to 15-mL centrifuge tubes and taken to dryness. Diazoethane (3 mL) and 10 μ L of 1:3, HCl:ethanol, were added. Samples stood for 15 min until the yellow color disappeared, then were concentrated with a nitrogen evaporator to 0.5 mL. Samples were brought to final volume with ethyl acetate and analyzed for DCPA by GC (HP 5890A) equipped with a mass selective detector (HP 5970), operated in selective ion mode, and a 12 m by 0.2 mm methyl silicone column operated in splitless mode. The carrier gas (He) flow rate was 0.68 mL min^{-1} . Injector and transfer line temperatures were 275 and 250°C, respectively. Column temperature was initially held at 50°C for 2.5 min and increased to 250°C at $30^\circ\text{C min}^{-1}$ and held for 5 min. Mean recovery of DCPA from filter samples was $73 \pm 7\%$.

Soil and Vegetation

Residues of DCPA, MTP and TPA were extracted from 50-g soil samples by shaking for 2 h with 200 mL acidic acetone. A 50-mL aliquot was treated with 50-mL 0.8N NaHCO_3 and adjusted to pH 10 using 5N NaOH. The sample

was then extracted twice with 50 mL of petroleum ether in a separatory funnel and the aqueous phase set aside. Combined ether extracts were rotoevaporated, dissolved in toluene, reduced to a 5-mL volume on a water bath under a stream of nitrogen and analyzed for DCPA by GC as below.

The aqueous phase solution was adjusted to pH 1 with 10 to 15 mL of 10N H_2SO_4 and extracted twice with 50 mL 1:1 petroleum ether:diethyl ether. Ether extracts were combined, rotoevaporated, treated with diazopropane to form propylated derivatives of MTP and TPA, dissolved in toluene and reduced to 5-mL volume. Samples were then analysed for MTP and TPA with a Varian 6000 GC equipped with an electron capture detector and a 50 m capillary column (HP, Ultra 1, cross-linked methyl silicone gum) operated at a split ratio of 1:20. The column temperature was initially held at 245°C for 2 min and then increased at a rate of 2°C min⁻¹ to a final temperature of 265°C and held for 6 min. Injector and detector temperatures were 250 and 300°C, respectively. Mean recoveries from soil were 91 ± 9, 101 ± 15 and 97 ± 14% for DCPA, MTP, and TPA, respectively.

Dislodgeable residues of DCPA, MTP, and TPA were extracted three times from the surfaces of onion and parsley foliage samples with approximately 100 mL of aqueous Sur-ten solution. DCPA and some MTP residues were removed from the Sur-ten solution (pH 5) three times by adding 40 g of NaCl, shaking for one min with 50 mL of methylene chloride in a separatory funnel, and draining the methylene chloride layer through sodium sulfate. The remaining MTP and TPA residues were removed from the Sur-ten solution by adding H_2SO_4 to pH 1 and extracting with 1:1 petroleum ether:ethyl ether. Both the methylene chloride and ethyl ether extracts were treated with diazopropane to form derivatized MTP and TPA and analyzed by GC as for soil samples. Mean recoveries for dislodgeable residues on onions and

parsley were 90 ± 11 and $91 \pm 13\%$ for DCPA, 99 ± 1 and $90 \pm 13\%$ for MTP, and 95 ± 15 and $89 \pm 29\%$ for TPA, respectively.

Internal residues were extracted from foliage (after Sur-ten treatment) by mixing with 250 mL of a 1:19(v/v) mixture of 10N H_2SO_4 :acetone in a high speed blender. Extraction and analysis were performed as above for soil samples. Mean recoveries for internal residues from onions and parsley were: 91 ± 10 and $97 \pm 12\%$ for DCPA, 88 ± 13 and $101 \pm 16\%$ for MTP, and 98 ± 12 and $98 \pm 19\%$ for TPA, respectively.

RESULTS AND DISCUSSION

Drift and Volatilization

Residues of DCPA were found in downwind air samples on every sampling day (Table 2). Maximum concentrations were detected one day after application following the first irrigation. Residues were found on both resin and filter samples indicating that DCPA moved off-target in the vapor phase and on particles (Table 2). The ratio of filter to total concentration (F:T) was generally higher when the plot was dry vs immediately after irrigation. A Mann Whitney U test (Siegel 1956) was conducted on the F:T ratio for irrigated and non-irrigated days. A U of 2 was calculated and has a probability of random occurrence of 0.002, indicating that the two groups have significantly different F:T ratios. The higher F:T ratio on non-irrigated days indicated that soil particles contributed significantly more DCPA residues to the total atmospheric concentration when the field was dry than when wet. Under wet soil conditions, the predominant mechanism of off-target movement appeared to be through the vapor phase.

Volatilization of DCPA from the circular plot was also influenced by soil moisture (Fig. 2). On days 1 and 2 when the soil was moist, flux rates were an order of magnitude higher than on days 0 and 3 when the field had not been irrigated. Flux measurements taken 4 through 14 d after application when the field was wet, remained above $2.8 \text{ g ha}^{-1} \text{ h}^{-1}$. On day 21, the flux rate dropped to $1.3 \text{ g ha}^{-1} \text{ h}^{-1}$ as the field dried out. The importance of soil moisture on pesticide flux rates has been noted previously (Taylor et al., 1977; Glotfelty et al., 1984). Flux results from the mass movement of pesticides in soil water as it evaporates from the soil surface (Harper et al., 1976). This mass movement, termed "wick

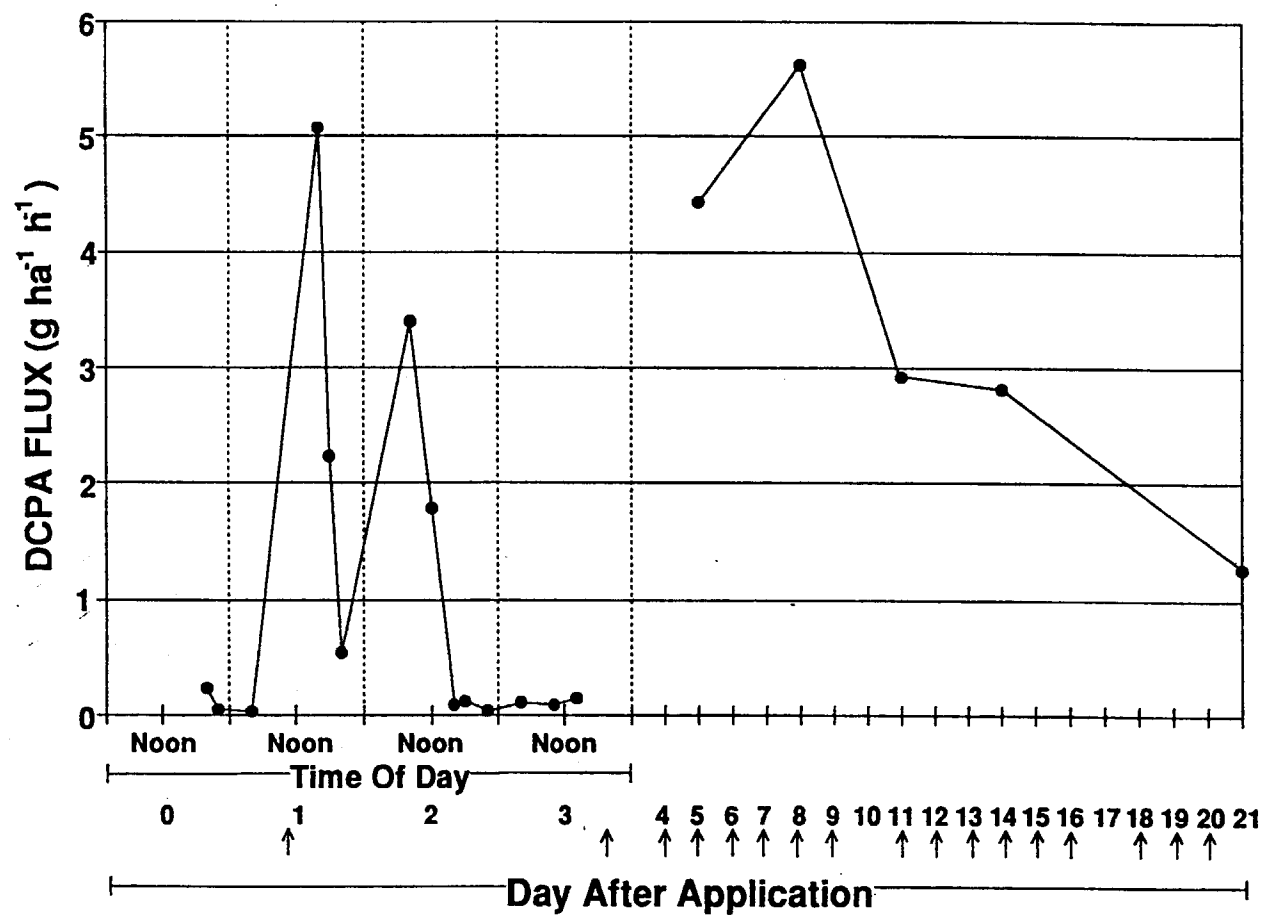


Figure 2. Volatilization flux of DCPA after application. Arrows indicate when the plot was irrigated.

Table 2. Concentrations of DCPA in air 30 m downwind from the circular plot.

Day ^a	Time ^b	Irrigation ^c	Concentration (ng m ⁻³) ^d			Ratio of F:T ^e
			Resin	Filter	Total	
0	0835		290	420	710	0.59
0	1030		35	150	185	0.81
0	1315		71	48	119	0.40
1	1230	X	910	100	1010	0.10
1	1720	X	260	41	301	0.14
2	1000		150	52	202	0.26
2	1400		22	18	40	0.45
3	1350		47	210	257	0.82
4	1510	X	200	120	320	0.38
8	1030	X	320	24	344	0.07
11	1240	X	61	6	67	0.09
14	1100	X	270	49	319	0.15
21	1014		33	15	48	0.31

a. Days after application.

b. Time air sampling began.

c. An X indicates that irrigation occurred just prior to air sampling.

d. Concentrations are an average of two replicate samples except on day 1 at 1230 where the concentration is from a single measurement.

e. Ratio of filter to total concentration.

evaporation" by Hartley (1969), can be driven by solar energy (Glotfelty et al., 1984). The maximum flux rate was $5.6 \text{ g ha}^{-1}\text{h}^{-1}$, close to the maximum found for DCPA by Glotfelty et al., (1984) of $8 \text{ g ha}^{-1}\text{h}^{-1}$ in a Maryland field study. Extrapolating over 21 d after application by averaging data points around missing values, an estimated 700 g ha^{-1} of DCPA was lost during daylight hours as a result of volatilization alone, or about 10% of the total applied. This is a rough estimate because flux determinations were only made on 9 of the 21 d (see Appendix III for calculations).

Off-target Deposition

During application both soil screens and potted parsley plants contained DCPA residues at 3 and 23 m from the circular plot (Table 3). Residues were higher in the southern direction corresponding to the predominant wind patterns during application. When unexposed soil screens and potted parsley were placed at the same locations after application, residues were also observed on them, correlating in magnitude with the prevailing winds (i.e. the north - south direction). The total mass deposited off target from 5 through 10 d after application was 3.9 g ha^{-1} , calculated from soil screen residues (see Appendix IV for calculations). Deposition of DCPA off-target could be through dry deposition of particles as well as by absorption of vapors by soil (Smith 1981). Extrapolating to a 21 d period, (assuming a constant deposition rate) then adding the mass found on the day of application, an estimated 17 g ha^{-1} were deposited within a 23 m radius of the application site. This mass, compared with the vapor-flux mass of 700 g ha^{-1} , is very small. Even if we assume that all the DCPA deposited off-target was in the vapor phase, only 2% of the DCPA

Table 3. Concentrations of DCPA on soil screens (ng cm^{-2}) and potted parsley plants (ug kg^{-1} , fresh weight) at four compass points and two distances from the circular plot.

Sample		North		East		South		West	
Type	Day ^a	3 m	23 m	3 m	23 m	3 m	23 m	3 m	23 m
Soil									
Screen	-1	ND ^b	ND	ND	ND	ND	ND	ND	ND
	0	5	3	9	6	43	9	2	3
	0 - 5	-- ^c	--	--	--	--	--	--	--
	5 - 10	120	35	21	53	56	59	9	4
Potted									
Parsley	-1	ND	ND	ND	ND	ND	ND	ND	ND
	0	3	ND	260	ND	14,000 ^d	1200	ND	3
	0 - 5	430	87	180	62	600	170	140	24
	0 - 10	1100	380	620	160	2500	640	210	58

a. Day after application. After DCPA was applied on day 0, new soil screens and potted parsley plants were placed around the field after application and collected 5 and 10 days later (0 - 5 and 0 - 10, respectively). However, due to rain, soil screens were replaced on day 5 collected 5 days later (5 - 10).

b. None detected. Detection limit was 0.2 ug per sample.

c. Sample lost due to rain.

d. Sample may have been sprayed directly or otherwise contaminated.

volatilizing within 21 d of application deposited within 23 m of the circular plot. The remaining 98% might undergo long-range transport as vapor or small particles, and subsequently deposit further off-target via dry deposition or rain-out. Long range transport of a variety of pesticides has been well documented in the literature (Risebrough, et al., 1968; Lewis and Lee, 1976; Cohen and Pinkerton, 1966).

Residues of DCPA were found in both dislodgeable and internal fractions of potted parsley samples on the day of application. Since background samples did not contain DCPA, these results indicated that either parsley rapidly absorbed DCPA through the stomata, or washing with Sur-ten solution did not completely remove all surface deposits. Internal and dislodgeable residues were combined in Table 3 for discussion purposes.

Nine of the 24 DCPA concentrations found on potted parsley in this study were higher than the illegal residues reported on parsley in California from 1984 to 1986 (CDFA, 1984-6; Table 3). The rest were less than 310 ug kg^{-1} , the maximum concentration found by CDFA during routine monitoring, indicating that parsley planted within 23 m of a legal application of DCPA could easily contain similar DCPA residues. This contamination could occur by simple spray drift (as seen for soil screens and potted parsley exposed on day 0), and/or by post-application volatilization of DCPA (as seen for soil screens and potted parsley collected 5 and 10 d after application). In addition, since 98% of the DCPA lost to the atmosphere via volatilization did not deposit within 23 m of the circular plot, it is possible that a portion of these airborne residues could deposit on non-target crops further downwind.

Soil Residues

Three of the 8 background samples contained small amounts of DCPA (44 ppb or less) as this material had been applied to a portion of the plot three years earlier. Persistence of DCPA one year after application was reported previously (Miller et al., 1978) with indications that at cool temperatures (10 °C) degradation does not occur within 90 d (Peplowsky, personal communication, Fermenta Plant Protection Co., Mentor, OH). Cool temperatures exist in this region of California in winter, slowing degradation of DCPA, and perhaps account for the residues found in background samples. None of the background samples contained detectable levels of either degradation product.

Concentrations of DCPA ranged from an average 5800 ug kg⁻¹ on the day of application to 120 ug kg⁻¹ 336 d after treatment (Table 4). Degradation of DCPA occurs by hydrolysis of the ester linkages forming MTP and TPA (Gershon & McClure 1966). Degradation in soil was reported to be primarily via microbial activity with the possibility of simple chemical degradation contributing as well (Hurto et al., 1979, Tweedy et al., 1968). Concentrations of MTP rose slightly 63 d after application and then declined afterwards (Table 4). A steady increase in MTP was seen by Hurto et al., (1979) in a laboratory study conducted over 112 d. However, concentrations of MTP in the field did not exhibit this trend perhaps due to the subsequent formation of TPA, a process that was not observed in the laboratory (Hurto et al., 1979).

Initially, TPA residues were low or not detected, followed by a slight increase as DCPA degraded to MTP, with a subsequent decline towards the end of the study (Table 4). Iyer et al. (1969) saw a similar trend for

Table 4. Mean concentrations ($\mu\text{g kg}^{-1}$) of DCPA, MTP and TPA in soil and vegetation of the circular plot.

Day ^a	SOIL ^b			VEGETATION ^c		
	DCPA	MTP	TPA	DCPA	MTP	TPA
-1	12(21) ^d	ND ^e	ND	-- ^f	--	--
0	5800(1900)	28(10)	ND	--	--	--
1	7000(620)	21(10)	ND	--	--	--
7	5600(1400)	35(5)	4(5)	--	--	--
14	5600(1300)	38(9)	23(12)	--	--	--
21	4100(1400)	84(66)	490(790)	--	--	--
42	2900(1600)	31(17)	920(330)	620(280)	33(14)	64(29)
63	1800(710)	98(22)	810(350)	220(57)	14(11)	42(26)
84	1100(480)	15(18)	710(480)	120(54)	31(6)	44(18)
168	110(57)	ND	120(76)	--	--	--
217	220(71)	ND	53(42)	ND	ND	ND
336	120(29)	ND	22(17)	ND	ND	ND

a. Days after application.

b. Soil concentrations expressed on a dry weight basis.

c. Vegetation concentrations expressed on a fresh weight basis. Onions were sampled 42, 63 and 84 d after application while parsley was sampled 217 and 336 d after application.

d. Mean of 6 replicates with standard deviation in parentheses.

e. None detected. Detection limit was $20 \mu\text{g kg}^{-1}$ for all three compounds in soil and vegetation.

f. Sample not taken.

these degradation products in a laboratory study. The higher concentrations of TPA, as compared with MTP, and its persistence in soil beyond the time when MTP residues were no longer detected indicates that it is more persistent than MTP.

Residues of DCPA in soil sampled outside the circular plot ranged from none detected to 130 ug kg^{-1} (Appendix V). Concentrations found on each sampling date (including background) were not significantly different as tested by a ranked analysis of variance (Conover and Iman, 1981; Table 5).

In soil core samples, DCPA was found to a depth of 122 cm (4 feet), 21 d after application (Table 6). Residues were also found 91 cm (3 feet) deep, 84 d after application. Subsequently, DCPA was not detected below the soil surface. Miller et al. (1978) found DCPA residues down to 120 cm in a Panoche loam soil but did not detect it below 15 cm one year after application, concluding that DCPA movement was minimal. In addition, bioassays used in DCPA leaching studies indicated that it does not move below the surface layers (Menges and Hubbard, 1970; Menges and Hubbard, 1971). In California, DCPA has not been found in groundwater except for a possible point source contamination that occurred in a monitoring well (Brown et al., 1986; Ames et al., 1987; Cardozo et al., 1988). However, in potato growing regions of eastern Oregon, DCPA was found in shallow groundwater (Bruck 1986) indicating that under certain conditions groundwater contamination might occur.

Residues of MTP were not found below 15 cm after the initial sampling (Table 6). In contrast, TPA was detected below 15 cm, particularly 336 d after application where it was found at the 91 cm depth.

Table 5. Analysis of variance of the ranks of DCPA concentrations in surface soil from the outer plot.

Analysis of Variance of Ranked Data ^a					
Source	df ^b	Sum of Squares	Mean Squares	F value	Probability
Model	8	1568	196	0.84	0.572
Error	44	10260	233		
Total	52	11829			

Day ^c	Mean of Rankings ^d
84	36
14	33
63	30
7	29
42	27
21	27
-1	23
1	20
0	19

a. Dependent variable = ranks of DCPA concentrations in surface soil of the outer plot. Independent variable = day after application.

b. degrees of freedom.

c. Days after application.

d. Sample size (n) was 6 for all days except background (day -1) where n = 5.

Table 6. Concentrations ($\mu\text{g kg}^{-1}$, dry weight) of DCPA, MTP, and TPA in soil cores taken from the circular plot^a.

Day ^b	Depth (cm)	DCPA			MTP			TPA		
		C1 ^c	C2	C3	C1	C2	C3	C1	C2	C3
1	0-15	50	102	102	ND	ND	26	ND	ND	ND
	15-30	28	176	70	ND	52	ND	ND	ND	ND
21	0-15	2007	2820	627	ND	40	ND	669	33	144
	15-30	ND	393	ND	ND	ND	ND	ND	ND	ND
	30-46	ND	194	ND	ND	ND	ND	ND	ND	ND
	46-61	ND	ND	274	ND	ND	ND	ND	ND	59
	61-76	ND	158	ND	ND	ND	ND	ND	ND	ND
	76-91	ND	18	28	ND	ND	ND	ND	ND	ND
	91-107	ND	ND	26	ND	ND	ND	ND	ND	ND
	107-122	ND	30	ND	ND	ND	ND	ND	ND	ND
	122-137	ND	ND	ND	ND	ND	ND	ND	ND	ND
	137-152	ND	ND	ND	ND	ND	ND	ND	ND	ND
84	0-15	78	67	44	ND	ND	ND	410	289	1134
	15-30	30	ND	T(13) ^d	ND	ND	ND	111	97	121
	30-46	T(11)	ND	ND	ND	ND	ND	71	40	ND
	46-61	T(5)	ND	ND	ND	ND	ND	ND	ND	ND
	61-76	T(6)	ND	ND	ND	ND	ND	ND	ND	ND
	76-91	T(6)	ND	ND	ND	ND	ND	ND	ND	ND
	91-107	ND	ND	ND	ND	ND	ND	ND	ND	ND
	107-122	ND	ND	ND	ND	ND	ND	ND	ND	ND
	122-137	ND	ND	ND	ND	ND	ND	ND	ND	ND
	137-152	ND	ND	ND	ND	ND	ND	ND	ND	ND
168	0-15	22	38	99	ND	ND	ND	163	ND	164
	15-30	ND	ND	ND	ND	ND	ND	ND	ND	ND
	30-46	ND	ND	ND	ND	ND	ND	ND	ND	ND
	46-61	ND	ND	ND	ND	ND	ND	ND	ND	ND
	61-76	ND	ND	ND	ND	ND	ND	ND	ND	ND
	76-91	ND	ND	ND	ND	ND	ND	ND	ND	ND
	91-107	ND	ND	ND	ND	ND	ND	ND	ND	ND
	107-122	ND	ND	ND	ND	ND	ND	ND	ND	ND
	122-137	ND	ND	ND	ND	ND	ND	ND	ND	ND
	137-152	ND	ND	ND	ND	ND	ND	ND	ND	ND
336	0-15	22	ND	70	ND	ND	ND	ND	ND	ND
	15-30	ND	ND	ND	ND	ND	ND	ND	ND	25
	30-46	ND	ND	ND	ND	ND	ND	ND	ND	96
	46-61	ND	ND	ND	ND	ND	ND	ND	ND	165
	61-76	ND	ND	ND	ND	ND	ND	ND	ND	95
	76-91	ND	ND	ND	ND	ND	ND	ND	ND	35
	91-107	ND	ND	ND	ND	ND	ND	ND	ND	ND
	107-122	ND	ND	ND	ND	ND	ND	ND	ND	ND
	122-137	ND	ND	ND	ND	ND	ND	ND	ND	ND
	137-152	ND	ND	ND	ND	ND	ND	ND	ND	ND

a. All segments in the three background cores were below the detection limit of $20 \mu\text{g kg}^{-1}$.

b. Days after application.

c. C1, C2, and C3 = core 1, core 2, and core 3, respectively.

d. T = trace. Concentrations below the detection limit (in parentheses) were quantified when possible.

Vegetation Residues

Concentrations of DCPA in and/or on onions ranged from 615 ug kg⁻¹ at initial sampling to 118 ug kg⁻¹ at harvest (Table 4), well below the tolerance level of 1000 ug kg⁻¹ (Code of Federal Regulations, 1987). Whether residues resulted from plant uptake of soil residues or by atmospheric scavenging by the onion foliage could not be determined from these data. However, plant uptake has been implied in studies conducted with carrots, radishes and pine seedlings (Gilbert and Lisk, 1978; Archer and Gauer, 1980; Iyer et al., 1969), indicating that DCPA might be taken up systemically in certain plants.

Parsley planted outside the onion plot also contained DCPA residues when sampled 63 d after application (64 d after seeding). Concentrations were 250, 80, 40, 72, 51, and 140 ug kg⁻¹ in sections 1 through 6 of the outer plot, respectively. In this case residues had to be from aerial transport of DCPA from the circular plot. The detection of DCPA on plants in the outer plot indicated that parsley seeded at the time of DCPA application can contain residues similar to those found by CDFA in routine monitoring, even though plants had emerged about 30 d after application.

In addition, parsley planted back onto the onion field immediately after harvest did not contain detectable residues of DCPA when sampled 217 and 336 d after application (Table 4). These data indicate that rotating parsley onto DCPA treated fields 126 d after application does not cause DCPA contamination under these conditions.

Mass Balance Budget

On the day of application, 89% of the DCPA applied was recovered in the media sampled (Table 7). The mass of DCPA recovered in surface soil of the circular plot declined exponentially with time. A 54-d, dissipation, half-life was calculated for this silty loam soil from the log-linear equation (Table 7). This is in close agreement with what Walker (1978) determined in the laboratory. In that study, with a constant soil temperature of 20 °C and 12% moisture content (values representative of average study conditions), a half-life of 40.5 d was determined.

Of the mass of DCPA lost in soil over 21 d (i.e. 2380 g ha⁻¹, Table 7), 29% of this loss was estimated to be due to volatilization, as determined from flux data. The large percentage of mass lost to volatilization indicates that the half-life calculated for DCPA is not a degradation half-life, driven solely by first-order decay. The agreement between the laboratory (Walker, 1978) and the field derived half-lives may therefore be purely coincidental. In addition, the r-squared for the log-linear equation was 0.86, leaving about 14% of the variability in DCPA mass over time, unexplained. Adding the mass of DCPA from all media sampled did not improve the r-squared (y intercept = 1.52 and regression coefficient = -0.140) further indicating that other processes, such as volatilization and leaching, that are not log-linear are not accounted for in this simplistic model.

Residues of MTP in surface soil on any given sampling date accounted for 1%, or less, of the total DCPA applied (Table 7). Residues of TPA were generally higher than MTP and on any given sampling date accounted for as much as 12% of the mass applied.

Table 7. Mass of DCPA, MTP and TPA (kg ha^{-1}) recovered in air, soil, and vegetation of the circular plot. A total of 7.08 kg ha^{-1} was applied on 9 April 1987.

a Day	Air ^b DCPA	Surface Soil ^c			Soil Core ^d			Vegetation ^{c,e}			Percent of applied
		DCPA	MTP	TPA	DCPA	MTP	TPA	DCPA	MTP	TPA	
0	1.3×10^{-3}	5.89	0.028	ND ^f				-- ^g	--	--	89
1	.012	6.04	0.019	ND	0.200	0.042	ND	--	--	--	86
7	.032	4.69	0.029	2.8×10^{-3}	--	--	--	--	--	--	67
14	.027	4.77	0.031	0.019	--	--	--	--	--	--	68
21	.012	3.51	0.070	0.42	0.751	ND	0.045	--	--	--	69
42	--	2.71	0.029	0.84	--	--	--	7.8×10^{-4}	4.1×10^{-5}	7.9×10^{-5}	51
63	--	1.61	0.086	0.71	--	--	--	1.9×10^{-3}	1.1×10^{-4}	3.7×10^{-4}	34
84	--	1.03	0.014	0.65	0.050	ND	0.346	6.2×10^{-3}	1.7×10^{-3}	2.4×10^{-3}	30
168	--	0.09	ND	0.10	ND	ND	ND	--	--	--	3
217	--	0.19	ND	0.05	--	--	--	ND	ND	ND	3
336	--	0.11	ND	0.02	ND	ND	0.320	ND	ND	ND	7
$\ln(\text{DCPA mass in surface soil}) = 1.48 - 0.0138(\text{Day}) \quad R^2 = 0.86$											

a. Days after application.

b. Data extrapolated to a 12-h period on Days 7, 14 and 21.

c. Mean of 6 replicates.

d. Mass summed over 15 to 152 cm (15 to 30 cm on day 1) and averaged over the three replicate cores.

Mass from 0 to 15 cm depth was not included because this would partially duplicate surface soil mass.

e. Onions were sampled 42, 63 and 84 d, and parsley on 217 and 336 d after application.

f. None detected. Detection limit was 20 ug kg^{-1} for all three compounds in soil and vegetation.

g. Not sampled.

The mass of DCPA recovered from soil cores was calculated using bulk density measurements (Table 8) multiplied by concentration and volume of each core segment to get mass per segment. The mass in each segment was then summed in each core (minus the top 15 cm), averaged over the three replicate cores per day and presented on a kg ha^{-1} basis (Table 7). The mass of DCPA in soil below 15 cm amounted to 11% of the mass balance budget on day 21 and subsequently declined (Tables 7 and 9). Residues of TPA found below 15 cm accounted for 4.5% of the total budget 336 d after application (Table 9). This mass (0.32 kg ha^{-1} , Table 7), amounts to 71% of the mass remaining on field, indicating that 336 d after application, most of the original DCPA applied is in the form of TPA residing in the soil column.

Residues of DCPA and the two degradation products in vegetation taken from the circular plot amounted to less than 1% of the total mass applied which is consistent with other research on pine seedlings using carbon-14 labeled DCPA (Iyer et al., 1969).

CONCLUSIONS

Off-target movement of DCPA in air occurs both during and after application. The highest concentrations in air downwind of the circular plot occurred one day after application when the field was first irrigated. Downwind air samples indicated that DCPA moved off-target as a gas and on particles both during and after application. Deposition of DCPA occurred off-site both during and after application as evidenced by residues found on soil screens and potted parsley placed up to 23 m outside the circular plot.

Table 8. Bulk density of soil in cores taken from the DCPA plot.

Depth (cm)	Bulk Density (g cm ⁻³)
0-15	1.35
15-30	1.51
30-46	1.52
46-61	1.37
61-76	1.29
76-91	1.27
91-107	1.30
107-122	1.38
122-137	1.40
137-152	1.41

Table 9. Percent of DCPA, MTP, and TPA mass recovered in soil cores.^a

Day ^b	% Recovered in Cores 0-152 cm				% Recovered in Cores 15-152 cm			
	DCPA	MTP ^c	TPA ^c	Total	DCPA	MTP ^c	TPA ^c	Total
1 ^d	5.5 ^e	0.9	ND ^f	6.4	2.8	0.6	ND	3.4
21	63	0.4	10	73.4	11	ND	0.6	11.6
84	2.1	ND	21	23.1	0.7	ND	4.9	5.6
168	1.6	ND	3.7	5.3	ND	ND	ND	ND
336	0.9	ND	4.5	5.4	ND	ND	4.5	4.5

a. Percent calculated as percent of DCPA applied (7.08 kg ha⁻¹). Data presented as the sum of segments 0 to 152 cm deep and 15 to 152 cm deep to illustrate the movement of material below the soil surface.

b. Days after application.

c. Expressed in DCPA equivalent weight.

d. Cores collected on day 1 were only 30 cm deep therefore data represent depths 0 to 30 and 15 to 30 cm.

e. This value believed to be low due to analytical difficulties encountered in the chemistry laboratory with this sample set.

f. All segments below the detection limit of 20 ug kg⁻¹.

An estimated 10% of the total DCPA applied was lost to volatilization over a 21 d period. Approximately 2% of the total DCPA lost by volatilization in 21 d was deposited within 23 m of the circular plot indicating that 98% of this material was available for further transport. In addition, an estimated 29% of the DCPA dissipated in soil 21 d after application was due to volatilization.

Results indicate that the primary mechanism of DCPA contamination in adjacent plots is from atmospheric transport both during and well after application. "Post-application drift" apparently occurs via the release of DCPA from the surface soil within the treated plot into the atmosphere, followed by transport and deposition of these residues to adjacent areas. The effectiveness of buffer zones as a means of controlling off-site deposition could not be determined from this investigation since samples were not taken beyond 23 m of the treated area.

Residues of DCPA and TPA were seen to leach to a small degree in this silty loam soil. However, 336 d after application DCPA was no longer detected below 15 cm while TPA was found to a depth of 91 cm. Residues of MTP were not detected below 15 cm after the initial sampling date.

Parsley planted back onto the circular plot within 126 d of a legal DCPA application did not contain detectable residues even though soil samples still contained small amounts of DCPA. Thus rotation of parsley onto fields previously treated with DCPA does not lead to contamination under certain field conditions.

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Appendix I. Meteorological and concentration data used to calculate DCPA flux from the circular plot.

RUN TIME	CONTINUOUS TIME	DAY	START TIME	<---cm/s--->		Temp	dT	UDir	Ri	Phi(m)	Phi(c)	<---µg/m3--->		FLUX (µg/m ² ·hr)	Total Dacthal Loss (g/plot/period)
				U30	U80							C30	C80		
2.00	10.00	9	1845	64.8	89.6	22.04	0.419	112.6	0.114	1.412	1.666	0.490	0.140	23.2	0.36
2.00	13.75	9	2130	40.9	59.0	14.03	0.187	106.9	0.098	1.368	1.589	0.181	0.077	5.4	0.09
6.80	15.00	10	0	58.0	76.3	10.19	0.296	66.1	0.153	1.512	1.838	0.145	0.073	3.0	0.16
2.00	30.00	10	1415	344.4	417.8	27.22	0.012	154.7	.000	1.002	0.889	2.510	1.530	508.2	7.98
2.00	32.25	10	1630	450.4	530.1	21.20	0.115	121.1	0.003	1.016	0.920	1.080	0.662	224.3	3.52
2.00	34.75	10	1900	242.7	294.9	17.49	0.208	175.3	0.013	1.064	1.023	0.565	0.385	54.3	0.85
2.40	46.50	11	*700	218.9	556.7	11.31	0.049	268.0	.000	1.000	0.886	0.368	0.226	340.4	6.42
3.00	49.50	11	1000	672.6	715.9	17.31	-0.472	275.4	-0.043	0.841	0.679	0.519	0.142	179.5	4.23
3.00	53.00	11	1330	477.4	570.2	22.49	-0.816	267.6	-0.016	0.928	0.786	0.016	0.005	8.7	0.21
3.00	56.50	11	1700	321.3	382.0	20.00	-0.058	273.5	-0.003	0.986	0.865	0.057	0.030	11.9	0.28
3.00	60.00	11	2030	131.3	170.9	11.14	0.414	247.5	0.045	1.200	1.286	0.048	0.025	3.7	0.09
7.00	63.50	11-12	2345	653.6	798.7	12.60	0.338	263.8	0.003	1.014	0.917	0.026	0.015	10.8	0.59
5.75	70.45	12	715	663.4	797.8	18.97	-0.548	271.3	-0.005	0.974	0.848	0.023	0.014	9.2	0.42
2.00	77.00	12	1330	491.1	584.5	26.85	-1.165	265.4	-0.022	0.905	0.756	0.042	0.025	14.8	0.23
6.00	122.50	14	1100	144.6	163.8	26.94	-0.298	187.7	-0.133	0.684	0.513	3.271	1.982	443.2	20.89
3.75	195.75	17	1215	498.2	584.7	24.43	-0.312	114.2	-0.007	0.966	0.837	1.728	0.892	562.5	16.57
6.50	267.50	20	1200	138.4	157.9	29.06	-0.409	211.7	-0.174	0.641	0.471	1.730	1.010	292.3	14.92
7.25	339.00	23	1115	340.4	395.9	24.69	-0.322	89.8	-0.017	0.922	0.778	1.260	0.681	281.5	16.03
7.00	505.25	30	930	509.2	602.6	20.11	-0.623	115.9	-0.012	0.943	0.806	0.394	0.230	126.6	6.96

Table key

Run time = duration of time air samples were taken.

Continuous time = cumulative time, in hours, after DCPA application commenced.

Day = date in April, 1987.

Start time = time of day that air sampling began.

U₃₀ and U₈₀ = wind speed at 30 and 80 cm, as determined by a linear regression equation using wind speeds taken at 20, 35, 55, 90, and 150 cm (see Seiber et al. 1989, for raw data).

Temp = temperature in °C, at 50 cm.

dT = difference in temperatures taken at 30 and 80 cm.

UDir = wind direction, in degrees, at a height of 2 m.

R_i = Richardson number (see Appendix I).

Phi_m and Phi_c = the diabatic correction functions (see Appendix I).

C₃₀ and C₈₀ = DCPA concentrations in air (µg m⁻³) at 30 and 80 cm, as determined by a linear regression equation using concentrations taken at 20, 35, 55, 90, and 150 cm (see Seiber et al. 1989 for raw data).

Flux = DCPA flux.

Appendix II. The aerodynamic method for calculating pesticide flux (Majewski et al., 1989).

$$P = \frac{k^2 (c_1 - c_2) (u_2 - u_1)}{\phi_c \phi_m [\ln(z_2/z_1)]^2}$$

where:

P = vertical pesticide flux ($\mu\text{g m}^{-2}\text{h}^{-1}$).

k = von Karman's constant (dimensionless and is approximately 0.4).

c_1 and c_2 = pesticide concentrations in air ($\mu\text{g m}^{-3}$) at heights z_1 and z_2 , respectively. z_1 and z_2 are measured in meters.

ϕ_c and ϕ_m are the diabatic functions for pesticide and momentum, respectively and have been defined by Pruitt et al. (1973) as :

For unstable conditions ($R_i < 0$):

$$\phi_c = 0.885(1-22R_i)^{-0.40}$$

$$\phi_m = (1-16R_i)^{-0.33}$$

For stable conditions ($R_i > 0$):

$$\phi_c = 0.885(1+22R_i)^{+0.40}$$

$$\phi_m = (1+16R_i)^{+0.33}$$

where R_i = Richardson number, an atmospheric stability parameter defined as:

$$R_i = \frac{g (dT/dz)}{T (du/dz)}$$

where:

g = acceleration due to gravity (9.81 m sec^{-2}).

T = air temperature in K.

dT = the difference in temperatures taken at 30 and 80 cm.

dz = the difference in heights (above) in meters.

du = difference in wind speeds (m sec^{-1}) at 30 and 80 cm.

Appendix III. Calculation of the mass of DCPA lost to the atmosphere by volatilization flux.

Date ^a	Day ^b	Run Time ^c	Total Run Time per Day	g plot ⁻¹ per period ^d	g plot ⁻¹ per day ^e
9	0	2.00	4.00	0.36	1.35
9	0	2.00		0.09	
10	1	6.80	12.80	0.16	11.73
10	1	2.00		7.98	
10	1	2.00		3.52	
10	1	2.00		0.85	
11	2	2.40	14.40	6.42	9.35
11	2	3.00		4.23	
11	2	3.00		0.21	
11	2	3.00		0.28	
11	2	3.00		0.09	
12	3	7.00	14.75	0.59	1.01
12	3	5.75		0.42	
12	3	2.00		0.23	
13	4	-- ^f	--	--	21.39 ^g
14	5	6.00	6.00	20.89	41.78
15	6	--	--	--	47.40
16	7	--	--	--	47.40
17	8	3.75	3.75	16.57	53.02
18	9	--	--	--	40.28
19	10	--	--	--	40.28
20	11	6.50	6.50	14.92	27.54
21	12	--	--	--	27.035
22	13	--	--	--	27.035
23	14	7.25	7.25	16.03	26.53
24	15	--	--	--	19.23
25	16	--	--	--	19.23
26	17	--	--	--	19.23
27	18	--	--	--	19.23
28	19	--	--	--	19.23
29	20	--	--	--	19.23
30	21	7.00	7.00	6.96	11.93
				Total	550.45

$$550.45 \text{ g plot}^{-1} \div 0.7854 \text{ hectares in the plot} = 700.85 \text{ g ha}^{-1}$$

a. Date in April.

b. Day after application.

c. Run time = air sampling interval in hours (see Appendix I).

d. g plot⁻¹ per period = mass volatilized from the plot during the sampling interval.

e. 12-h g plot⁻¹ per day = mass volatilized from the plot, on a 12 hour (daylight) basis. On days when more than one sample collected, the g plot⁻¹ per period were summed, then extrapolated to a 12 hour period using the total run time for the day.

f. Sample not taken.

g. Values reported on days when flux samples were not taken were calculated by averaging the data points generated before and after the missing value. For example, day 4 was calculated by averaging 1.01 and 41.78.

Appendix IV. Method used to calculate the mass of DCPA deposited to the outer plot using soil screen data from Table 3.

Area Calculations (Refer to Figure 1)

Circular plot radius = 50 m.....Area₁ = $\pi(50)^2 = 7854 \text{ m}^2$
 Radius of plot 3 m from the edge of the circular plot....Area₂ = $\pi(53)^2 = 8825 \text{ m}^2$
 Radius of plot 23 m from the edge of the circular plot...Area₂ = $\pi(73)^2 = 16,742 \text{ m}^2$

Area of circular band between the edge of the circular plot and 3 m:

$$\text{Area}_2 - \text{Area}_1 = 971 \text{ m}^2 \text{ or } 9.71 \times 10^6 \text{ cm}^2$$

Area of circular band between 3 m and 23 m outside the circular plot:

$$\text{Area}_3 - \text{Area}_2 = 7917 \text{ m}^2 \text{ or } 7.917 \times 10^7 \text{ cm}^2$$

Area of circular band between the edge of the circular plot and 23 m:

$$\text{Area}_3 - \text{Area}_1 = 8888 \text{ m}^2 \text{ or } 0.8888 \text{ ha}$$

Mass Calculations (see Table 3 for soil screen data)

(average soil screen concentration (ng cm⁻²) x area (cm²) x 10⁻⁹ = g of DCPA)

Day 0 (day of application)

<u>3 m</u>	<u>23 m</u>
14.75 ng cm ⁻² x (9.71 x 10 ⁶ cm ²) x 10 ⁻⁹ = 0.14322 g	5.25 ng cm ⁻² x (7.917 x 10 ⁷ cm ²) x 10 ⁻⁹ = 0.41564 g

Days 5 to 10

51.5 ng cm ⁻² x (9.71 x 10 ⁶ cm ²) x 10 ⁻⁹ = 0.50006 g	37.75 ng cm ⁻² x (7.917 x 10 ⁷ cm ²) x 10 ⁻⁹ = 2.99875 g
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Mass recovered on day of application = 0.14322 + 0.41564 = 0.55886 g

Mass recovered days 5 to 10 = 0.50006 + 2.99875 = 3.49881 g

Extrapolating to days 1 -21 = (3.49881 ÷ 5) x 21 = 14.695 g

Adding the day of application = 14.695 + 0.55886 = 15.25 g (mass recovered 0 to 21 d)

On a per hectare basis = 15.25 g ÷ 0.8888 ha = 17.16 g ha⁻¹

Appendix V. Concentrations of DCPA, MTP, and TPA ($\mu\text{g kg}^{-1}$, dry weight) in surface soil inside and outside the circular plot.

Day ^a	Section ^b	Inside			Outside		
		DCPA	MTP	TPA	DCPA	MTP	TPA
0	1	9021	44	ND ^c	ND	ND	ND
	2	5387	36	ND	36	ND	ND
	3	4547	20	ND	ND	ND	ND
	4	6788	27	ND	26	ND	ND
	5	5442	24	ND	21	ND	ND
	6	3644	16	ND	ND	ND	ND
1	1	7507	ND	ND	24	ND	ND
	2	6230	23	ND	18	ND	ND
	3	7112	31	ND	ND	ND	ND
	4	6908	18	ND	54	ND	ND
	5	6558	34	ND	ND	ND	ND
	6	7926	20	ND	ND	ND	ND
7	1	5717	37	11	37	ND	ND
	2	5209	30	10	50	ND	ND
	3	8269	38	ND	ND	ND	ND
	4	5531	40	ND	41	ND	ND
	5	4038	29	ND	26	ND	ND
	6	4840	39	ND	ND	ND	ND
14	1	6630	27	21	30	ND	ND
	2	5456	28	28	35	ND	ND
	3	7736	44	30	ND	ND	ND
	4	4926	37	29	86	ND	ND
	5	4400	40	29	47	ND	ND
	6	4664	50	ND	27	ND	ND
21	1	6216	203	97	41	ND	ND
	2	3255	81	2086	28	ND	ND
	3	2821	37	221	ND	ND	ND
	4	3739	29	220	31	ND	ND
	5	3132	45	263	37	ND	ND
	6	5388	110	54	ND	ND	ND
42	1	4385	43	1020	59	ND	ND
	2	580	ND	1403	34	ND	ND
	3	4258	43	582	ND	ND	ND
	4	2138	38	755	59	ND	ND
	5	1912	24	1168	ND	ND	ND
	6	4336	39	601	ND	ND	ND
63	1	1638	97	468	51	ND	23
	2	1504	69	1481	35	ND	ND
	3	1219	80	795	ND	ND	ND
	4	3112	115	686	36	ND	ND
	5	2220	96	807	38	ND	ND
	6	1354	128	607	ND	ND	ND
84	1	1249	20	645	35	ND	ND
	2	408	ND	158	43	ND	ND
	3	1641	41	1483	ND	ND	ND
	4	1531	29	886	134	ND	ND
	5	1228	ND	851	26	ND	ND
	6	681	ND	253	97	ND	23

Continued....

Appendix V, continued

168	1	85	ND	257	--- ^d	---	---
	2	87	ND	92	---	---	---
	3	93	ND	79	---	---	---
	4	205	ND	152	---	---	---
	5	147	ND	57	---	---	---
	6	44	ND	71	---	---	---
217	1	129	ND	59	---	---	---
	2	163	ND	85	---	---	---
	3	247	ND	ND	---	---	---
	4	279	ND	87	---	---	---
	5	210	ND	87	---	---	---
	6	318	ND	ND	---	---	---
336	1	80	ND	29	---	---	---
	2	81	ND	36	---	---	---
	3	136	ND	37	---	---	---
	4	148	ND	29	---	---	---
	5	126	ND	ND	---	---	---
	6	132	ND	ND	---	---	---

a. Day after application.

b. Sections numbered 1 through 6 as described in materials and methods.

c. None detected. Detection limit was 20 ug kg⁻¹ for all 3 compounds.

d. Sample not taken.